The Auto-Ignition of Fuels

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A Study of Auto-Ignition Temperatures

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III—(a) Mixtures of Pure Substances, (b) Gasolines[1,2]

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The auto-ignition temperatures of a number of mixtures of pure substances and gasolines of known knock rating have been measured. The mixtures selected represented a wide range of fuel characteristics and were chosen for their value in working toward the more complex mixtures represented by the gasolines. Three general types of curves showing the relationship between composition and auto-ignition temperature were obtained—one showing a minimum, another showing a maximum, and a third showing both a maximum and minimum. Straight-run gasolines show a regular relationship between knock rating and auto-ignition temperature, the auto-ignition temperature changing toward an optimum with improved knock rating. Cracked gasolines do not show a distinct relationship, but give a characteristic curve. The effect of lead tetraethyl is to raise or lower the auto-ignition temperature toward the optimum. A working hypothesis to correlate auto-ignition temperatures and knock is advanced.

[1] Presented by Mr. Hamilton as part of the Combustion Symposium under the title "Auto-Ignition Temperatures of Pure Substances, Binary Mixtures, and Gasolines" before the Divisions of Gas and Fuel Chemistry and Petroleum Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

[2] This paper forms part of the dissertation submitted by Mr. Hamilton in partial fulfilment of the requirements for the Ph. D. degree at New York University. Acknowledgment is made to the Altantic Refining Company which sustained this work through a fellowship.

AS THIS study is concerned primarily with an investigation of the relationship of auto-ignition temperature to knock or other characteristics of motor fuels, a brief review of this application may be presented.

To Constam and Schläpfer[1,*] and later Moore[2] are due credit for attempting to associate auto-ignition temperatures with the suitability of a fuel for use in the internal-combustion engine, especially of the Diesel type. Whereas the direct test in the engine gave information as to the suitability of the fuel for that particular type of engine, it was unsatisfactory from the standpoint of time required, ease of manipulation, cost, and control of the variables entering the test. Since ignition in the Diesel engine takes place as a result of the high temperature developed through adiabatic compression, it was evident that if the temperature attained was too low rapid combustion would take place when the liquid fuel was injected into the hot, highly compressed air in the cylinder. The important factor under consideration was the temperature necessary to ignite the fuel. From the equation

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

knowing the initial temperature, T_1, and the initial and terminal pressures, P_1 and P_2, the terminal temperature, T_2, could be calculated for any particular engine. If the temperature at which a given combustible liquid would ignite were known, then it could be readily determined, by applying the above formula to a given engine, whether or not a given liquid fuel would ignite properly in the engine. However, no data being available on the ignition temperature of such liquid fuels as were used in the Diesel engine, it was necessary to develop apparatus for a comparative test which would give the desired information. With the apparatus of Holm[3] for guidance, Moore[2] evolved a form of apparatus and technic suitable to his purpose, which has been followed more or less closely by all subsequent investigators except the authors. By means of his "ignition meter" Moore[2] determined the auto-ignition temperatures of a number of substances and from these temperatures estimated their suitability for use in the Diesel engine. The results so obtained were not directly comparable with performance in a given engine, but might be equated by means of a constant for each set of engine conditions. This, however, is disputed by Tausz and Schulte.[22] The work of Moore,[2] carried out less than twelve years ago, was the first positive attempt to determine the suitability of a fuel for use in the internal-combustion engine through a measurement of its auto-ignition temperature.

Although the authors originally undertook a study of auto-ignition temperatures for their abstract value, the suspicion or subconscious urging that there might be a relationship between the auto-ignition temperature of a gasoline for use in

* Numbers in text refer to bibliography at end of article.

an engine operating on the Otto cycle and its tendency to knock directed attention to the determination of the auto-ignition temperature of gasolines of known knock rating. That such a suspicion was not unfounded and had been conceived by others was shown by an examination of the literature. For example, Ricardo[4] states that one of the factors determining the tendency of a fuel to knock is the "self-ignition" temperature of the fuel-air mixture. Brown[5] has shown that

$$\frac{\text{Rate of pressure rise}}{\text{Absolute auto-ignition temperature}} = \frac{1}{\text{H. U. C. R.} \times \text{constant}}$$

The relationship of auto-ignition temperature to knock has also been discussed by Egerton and Gates,[6] Tanaka and Nagai,[7] Guiselin,[8] Ormandy and Craven,[9] Weerman,[10] and others. No data are available, however, on the auto-ignition temperature of gasolines whose knock ratings have been determined on an experimental engine according to some generally accepted procedure.

The study of the mechanism of combustion of gasolines and their peculiar behavior in the internal-combustion engine has always been confronted with difficulties of considerable magnitude. One can hardly hope to arrive at a satisfactory understanding of the complex reactions which take place when the characteristics of the raw material are so little known. When the exact composition of a given gasoline under investigation is not known, the experimental results will be difficult to interpret and more qualitative than quantitative. Obviously investigations should begin back among fundamentals by a study of pure substances, then known mixtures of pure substances, and thence to the more complicated mixtures as represented by gasolines. With that principle and in that spirit these researches have been undertaken. Previous papers[11] give the results of a study of the auto-ignition temperatures of a wide range of pure substances of practical or structural organic interest. Additions are constantly being made to this list, but sufficient data have been gathered to justify proceeding to the study of mixtures of varying degrees of complexity. The results of a study of some of these mixtures are here presented.

Experimental Procedure

The apparatus and procedure used are those previously described by the authors[11a] except that it was not found necessary to use auxiliary alternating current as a means of obtaining delicate temperature control.[11b]

Study of Simple Mixtures

A study of the auto-ignition temperature of simple mixtures is related not only to fuels such as are used in the internal-combustion engine but to many other fields as well. The widespread use of certain chemicals, such as carbon tetra-

chloride, to extinguish fires or to reduce the inflammability of various solvents has suggested the study of the effect of carbon tetrachloride upon the auto-ignition temperature of various inflammable liquids such as benzene. Egerton and Gates[12] found a lowering of 30° to 40° C. of the auto-ignition temperature of gasoline on the addition of carbon tetrachloride. According to this observation, gasoline (vapor-air mixture) might become more inflammable instead of less inflammable when carbon tetrachloride is added to it. The effect of knock inducers and suppressors is a question which has not been definitely decided. The consensus of opinion, among previous observers, is that in general knock inducers lower and knock suppressors raise the ignition temperature of a fuel,[13] but this statement is not without contradictions.[14] Egerton and Gates[6] state that the ignition temperatures of mixtures are usually closer to those of the lower igniting component. This statement is only partially confirmed.

The curves of Figure 1 indicate the effect of adding carbon tetrachloride and diethyl ether in varying amounts by volume to benzene. The addition of carbon tetrachloride to benzene gives results similar to those reported by Egerton and Gates[12] for gasoline. Carbon tetrachloride itself could not be caused to ignite in the apparatus at any temperature available (1000° C.). If it can be ignited at all, its auto-ignition temperature is well above 1000° C. The presence of 5 per cent by volume of benzene does not render it ignitible. However, when the concentration of benzene reaches 10 per cent by volume, the mixture ignites readily with a sharp flash at a temperature (68° C.) below the auto-ignition temperature of pure benzene. Based upon the properties of carbon tetrachloride, it is natural to assume that when added in increasing amounts there would be a rapid rise in the auto-ignition temperature and that the addition of a comparatively small amount would render the mixture non-ignitible.

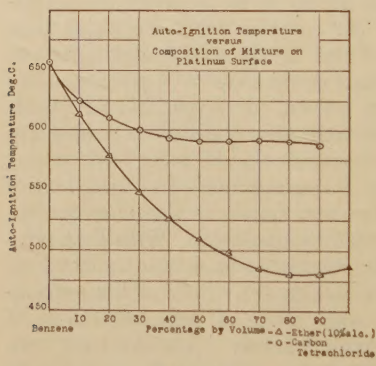

Figure 1

The fact that carbon tetrachloride containing 10 per cent of benzene has a lower ignition temperature than benzene is of significance in connection with the use of carbon tetrachloride in fire extinguishers, dry cleaners, etc., for such a mixture may be more inflammable than the pure substance even though it contains 90 per cent carbon tetrachloride. The addition of diethyl ether to benzene produces a similar,

but much more marked, effect. At a concentration of approximately 85 per cent by volume of ether and 15 per cent by volume of benzene a minimum auto-ignition temperature is obtained. Although carbon tetrachloride and diethyl ether have quite different properties, they both have the same general effect on benzene, both exhibiting a minimum auto-ignition temperature although the minimum in the case of benzene–carbon tetrachloride is not so pronounced. To what this minimum is due and its significance are at present matters of conjecture.

Figure 2 shows another type of auto-ignition temperature *vs.* composition curve. Both a maximum and a minimum are exhibited when acetic acid or *p*-xylene is added to absolute alcohol in increasing amounts. It is believed that this is the first time this type of curve has been observed. The fact that both a maximum and a minimum are obtained would seem to preclude any simple explanation. This cannot be due to any vapor pressure effect, as neither curve bears any relation to the vapor pressure curves of either mixture; nor can it be due to compound formation, solubility, or any other factor usually considered in the case of curves which exhibit abnormalities in properties which should otherwise be additive.

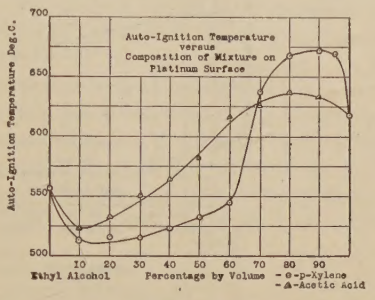

Figure 2

Edgar[15] has suggested the use of mixtures of normal heptane and isoöctane (2,2,4-trimethylpentane) as a means of rating motor fuels. He found that by using mixtures between the limits of 60 per cent normal heptane and 40 per cent isoöctane, and 40 per cent normal heptane and 60 per cent isoöctane the knock rating of any fuel could be expressed in terms of these mixtures. Figure 3 shows the auto-ignition temperature of mixtures of these two substances. Although similar in composition, structure, and vapor pressure, one of them, *n*-heptane, knocks readily in the engine while the other, isoöctane, is quite free from any such tendency. In this case the curve is quite regular. This relationship is of some significance in correlating knock and auto-ignition temperature, as the auto-ignition temperatures are nearly additive as in the case of knock rating.

Relation of Auto-Ignition Temperatures to Detonation

It has already been pointed out that many observers have suspected or noted a general qualitative relationship between auto-ignition temperatures and the detonating characteristics of fuels. For example, benzene is a fuel with a high

auto-ignition temperature (A. I. T.) (656° C. on platinum) and shows but little tendency to knock.[20] Diethyl ether, on the other hand, has a low A. I. T. (491° C. on platinum) and knocks badly in a motor.[20] On the basis of this and similar observations, it was assumed that fuels of high A. I. T. would show little tendency to knock while fuels of low A. I. T. would knock readily. Unfortunately, however, this simple relation-

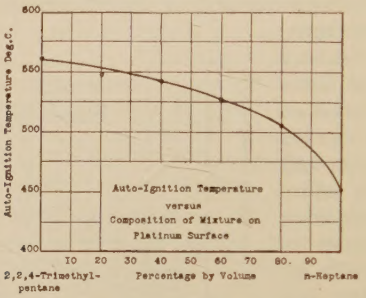

Figure 3

ship is not strictly correct, as many substances do not occupy their proper place on a curve relating A. I. T. and knock rating. In an attempt to arrive at any definite relationship between A. I. T. and knock, the authors have been somewhat handicapped by two facts. First, the knock rating of a number of pure substances is unknown to the authors, no comprehensive list having been published in the literature. Second, such knock ratings as have been

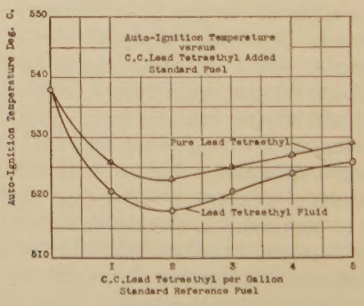

Figure 4

published are dependent on the test condition.[16,17,18] However, the data of Ricardo[4] have shown that ethyl alcohol is the best fuel in the list of pure substances given. The A. I. T. of ethyl alcohol is 557° C. It appears from a comparison of the list of A. I. T. already published[11] with the results of Ricardo that pure substances have a maximum antidetonating value when the A. I. T. is in the vicinity of 557° C. Accordingly, in the series benzene-toluene-xylene we might ex-

pect xylene (618° C.) to detonate less than toluene (633° C.), which in turn might be expected to detonate less than benzene (656° C.). Such an order seems to hold for any given series of homologous compounds, but it cannot be used accurately to compare substances that are not closely related in structure and properties. In the *n*-hydrocarbon series the order would be reversed—i. e., pentane would show the least tendency to knock, followed by hexane, heptane, etc. However, the absence of published data on the detonating characteristics of pure substances makes it impossible to confirm the above deduction or arrive at generalizations evaluating knock and A. I. T. of pure substances. It is postulated, however, that in any homologous series the A. I. T. and the knock rating will pass through or move toward or away from a maximum or minimum as one moves up or down the series. It is also postulated that the curve of A. I. T. versus number of carbons will parallel the curve of knock rating versus number of carbon atoms, or the A. I. T. curve

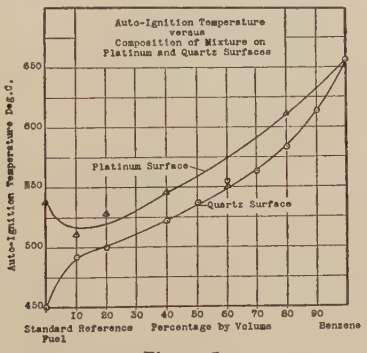

Figure 5

will be the mirror image of the knock curve. It is further postulated that for each series there will then be a critical A. I. T. corresponding to minimum knock, the knock increasing as we move either upward or downward away from this temperature. This specific critical A. I. T. corresponding to minimum knock will differ for each series and the difference will be a function of the dissimilarity of the series. Although the data for this broad generalization are scanty, the wide application of the Periodic Law and the observations of Boyd[19] offer some confirmation.

When representatives of two or more homologous series are present in a mixture, it seems practically impossible at present to predict the A. I. T. or knock of the mixture. Gasolines are complex hydrocarbon mixtures, the composition being unknown in most cases. They may also differ widely as to the structure of the individual components. Whereas the knock ratings of pure substances are not available, gasolines whose knock rating has been determined according to certain relative standards for a given engine and conditions

are available. If there is any relation between knock rating and A. I. T. it should manifest itself in the form of a simple curve. If the gasoline is composed of members of widely different series, then the A. I. T. would not necessarily be related to the knock by any simple curve.

Determination of Knock Rating

A number of gasolines of varied composition were obtained and their knock ratings determined as follows: A modified one-cylinder Lockwood-Ash engine, compression ratio 7:1, equipped with a Prony brake, tachometer, and special carburetor to give a constant fuel-air mixture over a wide range of throttle opening, was used. The engine was run at constant speed (1200 r. p. m.) with the intake air preheated to 60° C. and the cylinder jacket outlet water temperature maintained at 68° C. First a reference fuel (a straight-run midcontinent gasoline) was run in the engine. The throttle was slowly opened until an audible knock was heard. A mercury manometer, with an arbitrary scale and attached to the intake air line, was used to measure the throttle opening. Immediately after the reference fuel had been run, the

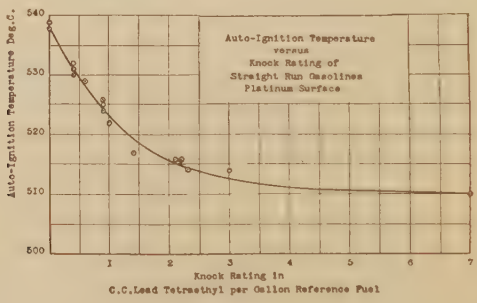

Figure 6

carburetor was drained and filled with the fuel to be tested. The throttle was again opened slowly until the unknown fuel knocked with the same intensity as the standard reference fuel. The observed manometer scale reading of the unknown fuel was subtracted from that of the standard and the difference was then translated to percentage of benzene or cubic centimeters of lead tetraethyl per gallon which must be added to the reference fuel to cause it to knock at the same throttle opening as the unknown fuel. This translation was effected by means of a throttle calibration curve which had been previously determined by actually adding benzene or lead tetraethyl to the standard fuel and evaluating the blended fuels as described for the unknown fuel.

Effect of Benzene and Lead Tetraethyl on Reference Fuel

As blends of the standard reference fuel with benzene or lead tetraethyl are used to express the knock rating of un-

known fuels, it is of distinct interest to ascertain how the I. A. T. of the reference fuel varied with the addition of benzene and lead tetraethyl in increasing amounts. Figure 4 shows the effect on the A. I. T. of adding various amounts of pure lead tetraethyl and lead tetraethyl fluid (lead tetraethyl in ethylene dibromide). In the case of the lead tetraethyl fluid the amount taken is expressed in terms of pure lead tetraethyl. The surface used was platinum-lead alloy. It will be observed that lead tetraethyl dissolved in the ethylene dibromide has a greater effect on the A. I. T. of the standard fuel than the same amount of pure lead tetraethyl. Egerton and Gates[12] have shown that the decomposition products of the lead tetraethyl are more effective than pure lead tetraethyl itself. Both curves show a distinct minimum at about 2 cc. of lead tetraethyl and are practically parallel over the essential portions. It is important to note that, contrary to Egerton and Gates, the effect of lead tetraethyl is to lower and then raise the A. I. T. of the fuel, but within the range plotted it did not raise the A. I. T. to the original value for the pure fuel. However, a concentration of 250 cc. lead tetraethyl per gallon gave an A. I. T. above that of the original fuel. It should be noted also that there is a tendency for the curves to flatten out in a relatively narrow range of A. I. T. This effect of lead tetraethyl to bring the fuel to within a certain range of A. I. T. will be developed in subsequent curves.

Figure 5 shows the effect of adding benzene in increasing amounts to the standard fuel. Two types of surfaces were used—one, platinum, of high catalytic activity, and the other, quartz, of low catalytic activity. It has been pointed out in a previous paper[11] that the nature of the surface used is very important in measuring A. I. T., and that, all other factors being equal, the A. I. T. would be higher on surfaces of greater catalytic activity. This is illustrated in Figure 5. It has also been shown previously[16] that the catalytic effect is not the same for all substances. The same substance may give widely different A. I. T.'s on surfaces; for example, in the case of nitrobenzene the A. I. T. is 556° C. on platinum and 513° C. on silver. On the other hand, the results on two different surfaces may be identical, the A. I. T. of aniline on platinum and silver being identical at 620° C. The curves in Figure 5 illustrate this phenomenon. The standard reference fuel gives different A. I. T.'s on platinum and quartz,

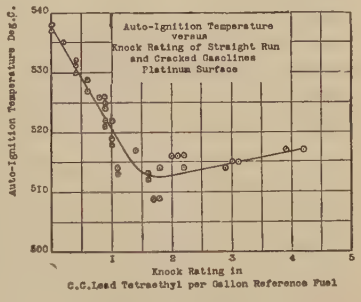

Figure 7

whereas benzene gives identical results on these surfaces. This accounts for the convergence of the two curves, but would not account for the minimum in the case of the platinum surface. It has frequently been observed that those substances which show the least tendency to detonate in the motor are least affected by change in the character of the igniting surface.

Auto-Ignition Temperatures of Straight-Run Gasolines

The A. I. T.'s of a number of straight-run gasolines were determined and compared with their knock ratings determined as described above. The gasolines were chosen at random, their only common characteristic being that they were all straight-run and conformed to the Navy specifications for motor gasolines. The resulting curve is given in Figure 6. The relationship is quite regular, the various points lying on a smooth curve. For gasolines of low knock rating, below approximately the equivalent of 2 cc. of lead tetraethyl per gallon, the curve is very nearly straight. It seems to be almost horizontal for high knock ratings, showing that the A. I. T. is less affected with increase in knock rating. The curve also approaches a minimum A. I. T. in the vicinity of approximately 510° C. As has been previously outlined, there exists for each homologous series a critical or optimum A. I. T. corresponding to a maximum of antiknock characteristics for that particular series. Apparently the optimum does not correspond to the same number of carbons for any particular series. The critical A. I. T. for the straight-chain normal saturated hydrocarbons is estimated to be approximately 500° C. (on platinum), which is below the critical A. I. T. for most gasolines.

Cracked Gasolines

A number of gasolines of widely different knock rating were procured from various sources and the A. I. T. on platinum of high catalytic activity of each was determined. The resulting curve is shown in Figure 7. In analyzing this curve a number of factors must be taken into consideration. The wide variation in composition of the gasolines and the many different series of saturated and unsaturated compounds present would be expected to result in a mixture or combination of many optima A. I. T.'s. However, since the influence of one series on another is as yet unknown, no predictions can be made as to specific effects. Furthermore, the inherent error in allowing for the catalytic effect of the surface must be considered because the effect is not constant for all series. Finally, there is a chance for error in measuring knock rating, especially as the fuel-air ratio does not remain constant over all ranges of throttle opening.[18] For these reasons it was not expected that the points would fall so as to make possible a smooth curve joining all of them.

Because of the wide scattering of the points, some difficulty was experienced in attempting to draw a curve which would be representative. When, however, a curve was drawn which had the points well distributed, it was found to bear resemblances to other curves such as are shown in Figures 4 and 5—i. e., the type of curve having a minimum. Samples of gasoline obtained from other laboratories, where different methods of measuring detonation are used, gave the same general type of curve.

Catalytic Effect of Surface on A. I. T. of Gasolines

In view of the marked effect of composition of the igniting surface on the A. I. T., it seemed desirable to determine the A. I. T.'s of a given set of gasolines using several different

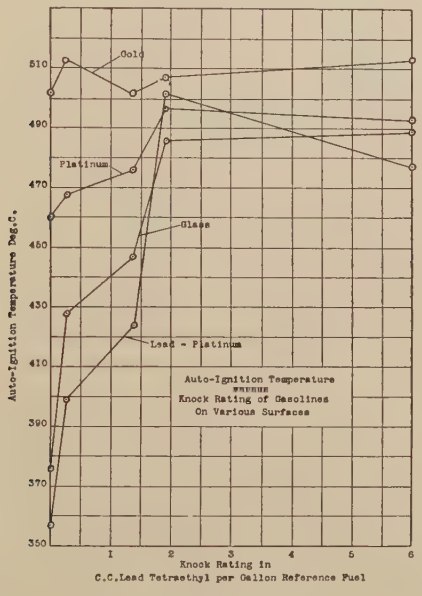

Figure 8

surfaces. The results of such a study are shown in Figure 8. The surfaces were selected on the basis of difference in catalytic activity as shown by previous experience. The gasolines were selected on the basis of wide differences in composition and were those prepared by the Texas Company and sent to various laboratories to be rated on the basis of knock. Their knock ratings were determined by the method previously described. The importance of the catalytic effect of various surfaces when studying gasolines is well illustrated by these curves. Gasolines that detonate readily are very sensitive to the catalytic effect of the igniting surface, whereas gasolines that do not detonate readily (that is, have a high knock rating) are but slightly affected by the nature of the surface.

As the knock rating improves the A. I. T. moves upward toward an optimum. The net effect is a series of curves which are concave downward and become horizontal in the region of the optimum temperature.

Effect of Lead Tetraethyl on Pure Compounds

Various investigators have shown that the effect of lead

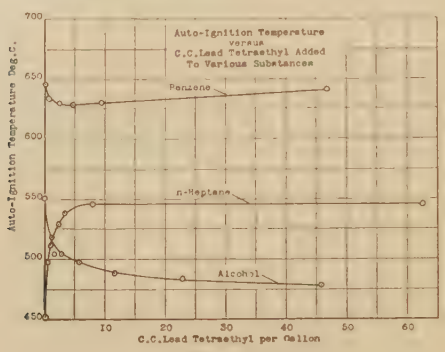

Figure 9

tetraethyl is to raise the A. I. T. of a given fuel. The effect of lead tetraethyl has already been shown in the case of gasolines. However, in view of the complex nature of gasolines and the fact that the A. I. T. obtained is only an average of the components present, it was decided to study the effect of lead tetraethyl on several pure liquids. The three liquids

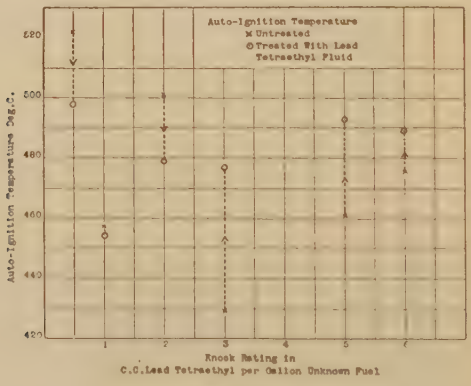

Figure 10

selected—benzene, *n*-heptane, and ethyl alcohol—were chosen because of their different A. I. T.'s, benzene has a high A. I. T., *n*-heptane a low A. I. T., while that of ethyl alcohol lies between the others. The results are shown in Figure 9. The effect of the addition of lead tetraethyl is to lower the A. I. T. of benzene and alcohol toward a minimum or opti-

mum temperature, while in the case of the *n*-heptane, the effect is to raise the A. I. T. toward an optimum. The effect here seems to be in good agreement with the general theory postulated.

Effect of Lead Tetraethyl on Gasolines

According to the experimental data thus far obtained, the effect of lead tetraethyl on a substance of high A. I. T. is to lower the A. I. T., while in the case of a substance of low A. I. T. the effect is to raise the A. I. T. It was decided, therefore, to study the effect of lead tetraethyl on gasolines of known knock rating. Six gasolines of widely different knock rating were obtained from the Ethyl Gasoline Corporation. The A. I. T. of each was determined. To each gasoline was then added sufficient lead tetraethyl to give it the same knock rating as the reference fuel—that is, to give equal antidetonation characteristics to all six. The results are shown in Figure 10. The effect of the lead tetraethyl on the first three gasolines (rated as fair) is to lower the A. I. T. while on the remaining three (rated as poor) the effect is to raise the A. I. T. This is in accordance with the action postulated, that the A. I. T. is raised or lowered toward the optimum, as the case may be, on addition of lead tetraethyl. As the gasolines are brought within the range of equal antidetonating characteristics, the A. I. T.'s are brought within an equally narrow temperature range.

Effect of Carbon Disulfide

As a motor fuel carbon disulfide has properties which have long puzzled students of detonation phenomena. It ignites very readily in air (149° C.) and pre-ignites badly in the motor,[20] but it does not detonate. When added to a motor fuel it acts as a knock suppressor.[20] Because of its interesting behavior, therefore, its effect on the A. I. T. of various substances was studied. The results of adding carbon disulfide in increasing amounts to benzene, ethyl alcohol, and ether are shown in Figure 11. The general shape of the curves for these three substances is as should be expected from the general theory; that is, the effect of the carbon disulfide is to change the A. I. T. toward an optimum temperature.

Discussion of Results

In determining the A. I. T. of a pure liquid the composition of the drop striking the igniting surface will have the same composition as the drop leaving the needle. The only change taking place will be in the size of the drop. As the time interval between leaving the needle and striking the surface is very small (less than 1 second), this change is probably extremely small. Again in passing through the heated zone, before striking the igniting surface, a slight thermal

decomposition may take place. However, this factor is probably also negligible in view of the small time interval.

In dealing with mixtures of liquids of widely different vapor pressures there exists the possibility that, owing to fractional distillation, the composition of the drop striking the surface will not be the same as that leaving the needle. As the change in A. I. T. with composition is being measured, this factor may become important, the extent to which this must be taken into consideration will depend on the combination of liquids. In the case of such mixtures as 2,2,4-trimethylpentane and *n*-heptane (Figure 3) it is negligible as both substances have practically the same vapor pressure; so it may be assumed that the drop suffered no essential change in composition in approaching the surface, and that the curve obtained is a true one for the conditions. With some gasolines this factor is probably more pronounced and does alter the curves. However, this effect is probably small

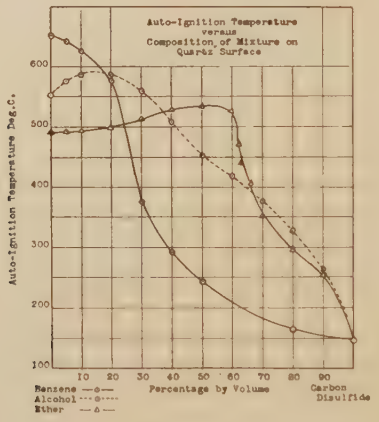

Figure 11

and not sufficient to affect the fundamental character of the curves. With other mixtures, especially those containing diethyl ether, the effect is probably greater, but nevertheless not enough to change the basic character of the curve.

It is fully realized in all this work that a very important factor—i. e., the fuel-air ratio—is apparently unknown. This is, however, not strictly so. The instant the liquid leaves the needle a film of vapor begins to form around the spheroidal drop. In approaching the igniting surface, through the heated zone, two processes are taking place—(1) increase in the thickness of the fuel vapor film surrounding the drop, and (2) diffusion of air (O_2) into the fuel film and diffusion of the fuel vapor (into the surrounding air O_2).

The condition of the system immediately prior to striking the igniting surface may be represented by Figure 12. In the figure, (1) represents the core of unvaporized liquid, (2) represents a series of layers of vapor too rich to ignite, (3) consists

of a series of layers whose composition is within the explosive limits for the system, and (4) is composed of a series of layers of films too lean to ignite. Upon striking the igniting surface layer (4) is displaced by impact with the surface, thereby exposing the series of films (3), which ignite. The heat of the reaction and that of the plate vaporize the core (1) and the high turbulence increases the diffusion causing the combustion of the remainder. During this period cracking unquestionably takes place, especially in the rich films. The time interval during which these series of reactions take place is so small that for all practical purposes, based upon numerous observations, the reaction may be considered instantaneous. Whereas the explosive limits vary with different substances, there is a fuel-air ratio of minimum ignition temperature.[13,21] Somewhere in the series of concentric films in region 3 such a fuel-air ratio exists. Assuming that the temperature of the films is nearly uniform, this film will accordingly be the first to ignite. Since the results reported are the lowest

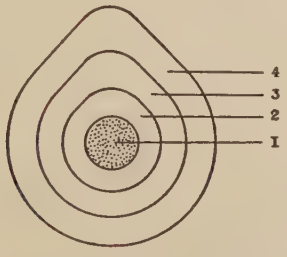

Figure 12—Condition of Drop Just before Striking Igniting Surface

temperatures at which a drop may be caused to ignite, it may be assumed that, within the limits of the apparatus, the A. I. T. reported will be approximately the ignition temperature of the fuel-air ratio of lowest ignition temperature. Whereas for many systems this ratio is unknown, the apparatus gives the temperature required to ignite such a ratio. As might be suspected, the ignition temperature of the fuel-air ratio of minimum ignition temperature will depend upon the composition of the igniting surface. This has been demonstrated in previous papers.[11] A comprehensive discussion of this phase of the subject, however, goes far into the field of catalysis, which is apart from the general purposes of this paper, and as it has already been discussed in a general manner,[11] nothing further need be added at this time.

Conclusions

1—The effect of lead tetraethyl is to raise or lower the auto-ignition temperature of pure substances and gasoline as toward an optimum auto-ignition temperature corresponding to decreased detonation characteristics.

2—Straight-run gasolines show a regular relationship be-

tween auto-ignition temperature and knock rating. The curve is a straight line in the range of greatest usefulness and interest.

3—Cracked gasolines do not show so regular a relationship, but give a characteristic curve similar to certain mixtures of pure substances.

4—For each homologous series there will be an optimum composition corresponding to a minimum knock rating. Similarly for each homologous series it is predicted there will be an optimum composition corresponding to minimum or maximum auto-ignition temperature, which in turn corresponds to minimum detonation characteristics. Some homologous series pass through a maximum and others through a minimum auto-ignition temperature. Depending on the nature of the series, this maximum or minimum auto-ignition temperature will correspond to minimum detonation characteristics. This accounts for the close relationship between knock and auto-ignition temperature in the case of straight-run gasolines. In the case of cracked gasolines, consisting of representatives of many homologous series, a number of optima will be represented giving rise to a concealed or complex critical auto-ignition temperature. This makes difficult the demonstration of a definite relationship between knock rating and auto-ignition temperature in the case of cracked gasolines.

5—In accordance with the above, the auto-ignition temperature will move upward or downward with improvement in knock rating through the addition of lead tetraethyl or other knock suppressors.

6—Lead tetraethyl fluid showed greater activity than pure lead tetraethyl.

7—Whereas the fuel-air ratio undergoing initial ignition is not known definitely, no attempt having been made to determine the same directly, nevertheless its ignition temperature is probably measured. The temperatures reported are thought to be the ignition temperatures of the fuel-air ratio having the minimum ignition temperature. Accordingly the term "auto-ignition" may be revised and "relative ignition temperature" substituted, the term "relative" being appropriate because the ignition temperature is dependent upon a number of factors which must be fully stated for each reported value.

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